Hierarchical Polybenzimidazole-grafted Graphene Hybrids as Supports for Pt Nanoparticle Catalysts with Excellent PEMFC Performance

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Abstract:

The inhomogeneous surface of state-of-the-art carbon supports leads to a weak Pt-C interaction and, thereby, the non-uniform dispersion of Pt nanoparticles and is responsible for the poor activity and stability of proton exchange membrane fuel cells (PEMFCs). In order to improve the surface uniformity, polybenzimidazole (PBI) has been covalently grafted onto both carbon black (Vulcan XC-72) and graphene by surface-initiated polymerization. Pt nanoparticles decorated on PBI-grafted carbon black and graphene show much narrower particle size distribution and smaller average particle size than on their pristine counterparts. Oxygen reduction reactions (ORRs) carried out on a rotating disk electrode (RDE) show the higher activity of Pt/PBI-XC72 and Pt/PBI-graphene than Pt/XC72 (ETEK-BASF) and Pt/graphene, respectively. With the insertion of negatively charged SO₃H-carbon black (FCB) between positively charged PBI-graphene sheets, the lamellar structure of the graphene becomes more expanded, further enhancing the ORR activity and giving rise to a higher mass activity of 183 mA/mg_{Pt} at 0.9 V vs. RHE on Pt/PBI-graphene + FCB than the 101 mA/mg_{Pt} of Pt/PBI-graphene and the 149 mA/mg_{Pt} of commercial Pt/XC72. The accelerated degradation testing (ADT) with transmission electron microscopy (TEM) characterizations demonstrated that the PBI functionalization helps to strongly anchor Pt nanoparticles on the surface of both

the carbon black and the graphene, which slows down the dissolution and migration/coalescence of the Pt nanoparticles during the durability tests. Furthermore, Pt/PBI-XC72 and Pt/PBI-graphene + FCB cathode catalysts have been applied in PEMFCs and they show encouraging mass activities in membrane electrode assembly (MEA) configuration. The **beginning of life** (BOL) MEA performance of the Pt/PBI-graphene + FCB shows a dramatic increase of the limiting current from ca. 500 mA/cm² to 2250 mA/cm², which further confirms the effective prevention of graphene restacking because of FCB insertion. In addition, the presence of the highly stable graphitic structure of graphene leads to the significant enhancement of durability during accelerated stress tests (AST) in PEMFCs: where the cell voltage at 1500 mA/cm² after 1000 cycles (1.0 V to 1.5 V) can be retained > 60% for Pt/PBI-graphene + FCB while for Pt/XC72, it decays more rapidly to 0 V. This study suggests the promise of using Pt/PBI-graphene + FCB hybrid cathode catalysts in fuel cells to achieve the DOE targets (i.e. < 30 mV loss at 1500 mA/cm² after 30 K potential cycling from 1.0 V to 1.5 V).

Highlights:

- Highly active and durable cathode catalyst supports have been developed.
- Homogeneous PBI functionalization on graphene surface results in very uniform Pt nanoparticles dispersion.
- Pt nanoparticles supported on hierarchical PBI-grafted graphene/carbon hybrids show improved catalytic activity and stability.
- Accelerated stress tests (AST) from 1.0 to 1.5 V demonstrated enhanced support stability in H₂-O₂ polarization.

Keywords: polybenzimidazole functionalized graphene; Hierarchical hybrids; proton exchange membrane fuel cells; support durability; accelerated stress test; catalyst performance

1. Introduction

Current energy and environmental issues urgently demand the use of renewable energy sources to replace conventional fossil fuels. Proton exchange membrane fuel cells (PEMFCs) have been regarded as one of the most promising renewable energy conversion technologies due to their high power density, high energy efficiency, and zero emissions. The performance of PEMFCs is dominated by the activity and durability of precious metal group (PGM) catalysts for oxygen reduction reactions (ORRs) occurring on the cathode side.[1, 2] There are several major challenges for the widespread commercialization of this fuel cell technology, including high cost, unsatisfactory activity, and low durability of PGM catalysts.[3] Although the development of Pt and Pt alloyed catalysts has made a great progress in recent years to improve the activity of the ORR while reducing the cost of the membrane electrode assembly (MEA), the durability of PEMFCs under steady and dynamic conditions remains a challenge. The degradation of the catalyst particles results in the loss of electrochemical active surface area (ECSA) and, consequently, causes the loss of the PEMFC performance. Two major mechanisms that attribute to the growth of Pt nanoparticles were proposed: Ostwald ripening (platinum oxidation/dissolution followed by re-deposition) and coalescence/agglomeration of platinum nanoparticles via nanoparticle migration on the surface of the carbon support.[1, 4-9] Carbon corrosion that has been reported earlier[10, 11] is also responsible for the migration, coalescence, and agglomeration of Pt nanoparticles over carbon supports because of the detachment of the catalyst nanoparticles as a result of the electrochemical oxidation of the carbon supports at higher operating voltages (>0.8 V). The extent by which the degradation of the cathode catalyst following the above possible processes depends largely on the interaction between the catalyst nanoparticles and the supporting materials as well as the surface chemistry of the catalyst supports. The most commonly used materials to support catalyst nanoparticles in low temperature PEMFCs are high surface area carbon blacks, e.g. Vulcan or Ketjen black. Continuous efforts are devoted to developing more durable catalyst supports; for example, we have successfully developed a series of carbon supports including functionalized carbon blacks,[12] steam etched carbon blacks,[13] and nanographite,[14] and concluded that higher carbon corrosion resistance is associated with a higher degree of graphitic structure. Recently, graphitized materials, i.e. carbon nanotubes,[15] graphitic carbon nitride,[16]

graphitic mesoporous carbon,[17] and activated carbon composite support[18, 19] have been reported to greatly overcome the carbon corrosion.

Graphene is the single-atomic-thick graphite layer in which each carbon atom forms three covalent bonds with the three neighboring carbon atoms using its three sp^2 electrons, and the fourth lone p_z electron will be shared by adjacent carbon atoms in the benzene ring to form a π bond[20]; hence, the carbon atoms in the graphene plane are “saturated,” relatively chemically inert and not prone to be oxidized. Graphene has many advantages over conventional carbon black catalyst supports, like high electronic conductivity, surface area, and mechanical strength, as well as excellent stability.[21] All of these unique properties make the graphene an ideal candidate for Pt catalyst support in PEMFCs;[22-29] it is expected that graphene-supported Pt catalysts would show significantly improved electrochemical stability as compared to carbon black-supported Pt catalysts. On the other hand, carbon black supports are generally inhomogeneous in terms of the morphology, surface energy/activity, and chemical composition. There are edges, ditches, steps and basal planes on the surface of carbon black along with the randomly distributed functional groups, such as phenol, carbonyl, carboxyl, and quinones, etc.;[30] while on graphene, though relatively morphologically smoother than carbon black due to its 2-D structure, there are still crumbles found on the edges after it is synthesized following the chemical reduction of graphene oxide.[31] These non-uniform defects of a lower coordinate number on the surface of the carbon supports will have a higher energy that prefers the nuclei formation of the Pt precursor ions and the particle landing from the Pt precursor reduction processes. Moreover, Pt nanoparticles can come into direct contact with the carbon supports, where the interactions between them are considered to be of an electric nature, meaning the electrons would shift either toward or away from the Pt atoms that landed on the carbon surface and will vary depending on the surface energy distribution across the surface of the carbon supports. The regions of weaker interaction strength are more likely to observe the migration of Pt particles during fuel cell operations. In this regard, chemically-functionalized graphene is of great interest. Uniform decoration of functional groups on the surface of carbon-based supporting materials could improve the chemical and energetic homogeneity of the carbon surface, resulting in the strong anchoring of catalyst particles. To allow for a better dispersion of the Pt nanoparticles, Pt nanoparticle

coalescence must be minimized, and the carbon corrosion must be inhibited to improve the PEMFC performance.[12, 32-34]

Polybenzimidazole (PBI) is a kind of polymer with superior stability and high proton conductivity, up to 0.2 S/cm upon phosphoric acid doping, and has been widely studied as the proton exchange membrane in high-temperature PEMFCs.[35, 36] Recently, PBI-coated carbon has been prepared by physical adsorption of PBI onto carbon surfaces through π - π interaction.[33, 37, 38] These catalysts showed improved durability and high catalytic activity as compared to commercial Pt/XC72. However, the loading of PBI on carbon is relatively low and surface coverage could not be precisely controlled. In addition, the interaction between carbon and PBI is expected to be weak due to their physical mixing.

Our previous recent work demonstrated that covalently-grafted polyaniline on functionalized graphene exhibited enhanced electrochemical stability due to the enhanced synergistic interaction between graphene and polyaniline.[39] In this work, PBI covalently-grafted carbon black and graphene was successfully prepared, systematically characterized, and employed as novel supports for Pt nanoparticles. The uniform grafting of PBI can help to guide the nucleation of Pt nanoclusters, thereby greatly refining the deposition of Pt particles onto the surface of PBI-carbon black/graphene. Both Pt/PBI-XC72 and Pt/PBI-graphene show significantly improved activity and accelerated degradation test (ADT) durability for ORR on RDE tests compared with Pt/XC72 and Pt/graphene. When effectively composited with negative charged SO_3H -carbon black (FCB) in between the positively charged PBI graphene 2-D sheets, the expansion of the graphene lamellar structure can be achieved to allow the significant improvement of mass transport, resulting in a comparable activity realized on RDE and MEA in H_2/O_2 PEMFCs with commercially available Pt/XC72. The accelerated stress tests (AST) in PEMFCs demonstrate the dramatically higher durability of Pt/PBI-graphene + FCB than that of Pt/XC72, which suggests a strong interaction between PBI-grafted carbon supports and Pt nanoparticles in addition to the highly stable graphitic structure of graphene. This work is one of the earliest demonstrations for using graphene-based catalysts in H_2/O_2 PEMFC with promising activity and durability.

2. Experimental

2.1 Synthesis of Pt/PBI-graphene and Pt/Pt/PBI-XC72

Graphene oxide (GO) was prepared according to our previously published method.[40] To partially reduce GO and recover the *sp*² carbon structure, NaBH₄ was added to a 100 mL aqueous dispersion of GO (1 mg/mL). The dispersion was heated at 80 °C for 1h. This mildly reduced GO was then subjected to diazonium functionalization using 4-aminobenzoic acid, hydrochloric acid, and sodium nitrite. After centrifuging and rinsing with DI water several times, the obtained benzoic acid-functionalized mildly-reduced GO was re-dispersed in water. Hydrazine was then added into the dispersion and the reaction mixture was refluxed at 95 °C overnight under constant stirring, yielding benzoic acid-functionalized graphene. Subsequently, the benzoic acid-functionalized graphene, isophthalic acid, and 3,3'-diaminobenzidine were added into 115% polyphosphoric acid. The mixture was stirred at 150 °C for 1 h, and then heated to 190-210 °C overnight (for 16 h) under a nitrogen atmosphere. At the end of the reaction, the temperature was further raised to 220 °C, and the viscous solution was poured into ice water. Finally, the precipitated product was neutralized with an ammonium solution, washed with copious water and methanol, and dried in a vacuum oven at 80 °C. For the preparation of PBI-carbon black, Vulcan XC-72 carbon black was used instead of graphene and the procedures were the same as those for PBI-graphene.

The deposition of the Pt nanoparticles on the PBI-graphene or PBI-XC72 was carried out by the reduction of H₂PtCl₆ in an aqueous ethylene glycol (EG) solution. **The water to EG ratio was 2:3 (v:v).** First, the PBI-graphene/PBI-XC72 was added to an aqueous EG solution, and the dispersion was sonicated for 30 min, followed by the quick addition of aqueous EG solution of H₂PtCl₆·6H₂O. After the mixture was refluxed at 140 °C for 6 h, the solid materials were collected by filtration and washed with DI water and ethanol. The obtained solid (Pt/PBI-graphene or Pt/PBI-XC72) was dried in a vacuum oven. For comparison, Pt/graphene was prepared using graphene instead of PBI-graphene.

2.2 Physical Characterizations

The morphology was characterized by a JOEL JEM-2100F transmission electron microscope (TEM) and a JOEL-7800 field emission scanning electron microscope (FESEM). The particle size distribution was obtained based on randomly measuring more than 200

primary Pt nanoparticles excluding the agglomerations in TEM images. The X-ray photoelectron spectroscopy (XPS) spectra were recorded by a Kratos AXIS Ultra X-ray photoelectron spectrometer. Fourier transform infrared spectroscopy (FT-IR) spectra were taken by a Nicolet spectrometer. N₂ sorption/desorption measurement was carried out on a Quantachrome Autosorb iQ gas sorption analyzer, and the pore size distribution was calculated based on the NLDFT model assuming a slit-shape pore structure.

2.3 Electrochemical Characterizations

Electrochemical measurements were performed in a three-electrode electrochemical cell using a glassy carbon rotating disc electrode (RDE) (0.196 cm², Pine Instruments) as the working electrode. It was polished with a 0.3 μm alumina suspension followed by a 0.05 μm alumina suspension until obtaining a mirror-like finish. To prepare the catalyst ink, the prepared catalyst was suspended by sonication in an isopropanol/DI water mixture (1:4 v/v) with a 20 wt.% Nafion solution (5 wt.%, Ion Power, Inc.). A 10 μL Pt suspension was dropped onto the glassy carbon electrode and dried. The mass loading of Pt was estimated to be 3.4 μg_{Pt}/cm². A Pt wire (Pine Instrument) served as the counter electrode, and a reversible hydrogen electrode (RHE) (HydroFlex[®]) was used as the reference electrode. Electrochemical experiments were performed using the electrochemical potentiostat (VSP, Biologic, TN). All potentials cited in this work were normalized with respect to the reversible hydrogen electrode (RHE).

All experiments were performed at room temperature. Prior to electrochemical tests, the catalysts were electrochemically cleaned by cycling the potential between 0.05 and 1.2 V (vs. RHE) at 500 mV/s for 100 cycles in a N₂-saturated 0.1 M HClO₄. Cyclic voltammetry (CV) scanning from 0.05 V to 1 V (vs. RHE) at a 20 mV/s scan rate was then carried out for ECSA measurements. Polarization curves of ORRs on RDE were recorded by sweeping the potential from 0.2 to 1.2 V (vs. RHE) at a 20 mV/s scan rate in an O₂-saturated 0.1 M HClO₄ aqueous solution with a rotating speed of 1600 rpm. All mass activities were calculated based on the current density at a potential of 0.9 V vs. RHE and normalized by the mass loading of Pt on the RDE. Accelerated degradation tests (ADT) were performed by potential scanning between 0.6 V and 1.2 V vs. RHE at a scan rate of 20 mV/s in N₂-saturated 0.1 M HClO₄ for 1000 cycles

and CV curves were plotted after 0, 200, 400, 600, 800, and 1000 cycles to record the ECSA decay.

2.4 MEA fabrication and H₂/O₂ PEMFC tests

The MEA was fabricated employing catalyst-coated membrane (CCM) methods with Pt/XC-72 black (20 wt.%, ETEK, BASF) and Pt/PBI-graphene, Pt/graphene, and Pt/PBI-XC72 (30 wt.%, home-made) applied to the anode and cathode, respectively. The catalyst ink was prepared by mixing the catalyst powder and 2-propanol with a Nafion suspension (5 wt.%, Ion Power, Inc.) via ultra-sonication followed by high-speed sheer stirring for 40 min. Subsequently, the as-obtained catalyst ink was sprayed directly on the Nafion membrane of the H⁺ form (N212, Ion power Inc.) until a loading of 0.1 mg_{Pt}/cm² on both electrodes was achieved. For comparison, both anode and cathode electrodes incorporated with a Pt/XC-72 black (20 wt.%, ETEK-BASF) of 0.1 mg_{Pt}/cm² were also prepared. The MEA with an active cross-sectional area of 5 cm² was then hot pressed by two decals at 135 °C, 600 psig for 1.5 min and sandwiched in between two gas diffusion layers (25BC, hydrophobic microporous layer coated, SGL Group). MEAs made of Pt/PBI-graphene and Pt/PBI-XC72 cathode were immersed in 2 M H₃PO₄ aqueous solution for 24 h and dried before tests.

The **beginning of life** (BOL) performance of the MEA was tested on a fuel cell test system (Fuel Cell Technology, NM). High purity H₂ and O₂ (99.999%) were fed into anode and cathode chambers with a constant flow rate of 200 sccm and 400 sccm, respectively, at the same absolute back-pressure of 3 bars. The cell temperature was kept at 80 °C, and the relative humidity for both anode and cathode was 100%. Voltage-current (VI) polarization curves were recorded at the scanning current mode from open circuit voltage (OCV) to limiting current density with each step point held for 1 min. Accelerated stressed testing (AST) was performed followed a triangle sweep cycling between 1.0 V to 1.5 V at a scan rate of 500 mV for 0, 10, 100, 200, 500, and 1000 cycles with H₂ and N₂ supplied into the anode and cathode chambers, respectively, where the observed OCV should be lower than 0.1 V. During the cycling, the temperature and relative humidity were maintained at 80 °C and 100%, while both electrodes were decreased to the atmospheric back pressure. After each set of CV cycling, VI polarization curves were recorded following the BOL testing protocols introduced above, and

the normalized cell voltage at the current density of 1500 mA/cm² with respect to BOL performance was reported.

3. Results and discussion

Figure 1. (a) FT-IR of PBI, PBI- XC72, and PBI-graphene; and (b) XPS N 1s spectrum of graphene, XC72, PBI, PBI-XC72, and PBI-graphene.

PBI- XC72 carbon black and graphene were prepared by the surface-initiated polymerization approach as described in the experimental section.[41] To validate the successful grafting of PBI onto graphene and XC72 surfaces, FT-IR and XPS were utilized to characterize these samples. Figure 1 shows FT-IR spectrum of PBI, PBI-XC72, and PBI-graphene. The FT-IR spectrum of PBI exhibited characteristic peaks at around 684, 793, 1280, 1460, and 1620 cm⁻¹, corresponding to the aromatic C-H out-of-plane bending, the breathing mode of benzimidazole, the benzimidazole in-plane deformation, and the C-N stretching, respectively.[42, 43] Similar peaks can be observed in PBI- XC72 and PBI-graphene, indicating the successful functionalization of graphene and XC72 with PBI. XPS spectra of PBI shows two peaks at ca. 398.4 and 400.2 eV in the PBI, which are identified to be pyridinic and pyrrolic nitrogen on the PBI, respectively.[37] Such identical peaks also appear in the XPS of PBI-XC72. On the other hand, the XPS spectra of graphene shows a peak around 400 eV that corresponds to pyrazoline due to the reducing agent, hydrazine, used in the synthesis. In the XPS of PBI-graphene, the N 1s peak of pyrrolic nitrogen overlaps with the pyrazoline peak, while the peak at ca. 398.4 eV (pyridinic nitrogen) could be observed, indicating the presence of PBI. Based on the element analysis, the atomic compositions of Nitrogen are 3.0 at.% and 4.6 at.% on PBI-XC72 and PBI-graphene, respectively, as compared to 0 at.% on the pristine XC72 and 0.7 at.% on graphene.

Table 1. Elemental compositions of XC-72, PBI-XC72, PBI-XC72, graphene, and PBI-graphene (in atomic percent)

Sample	C (%)	O (%)	N (%)	N/C
PBI	81.9	6.8	11.2	0.137
XC-72	89	11	0	0
PBI-XC72	85.8	11.3	3.0	0.035
Graphene	87.3	12.0	0.7	0.008
PBI- graphene	84.2	10.5	4.6	0.055

Figure 2. (a) FESEM image, (b) TEM image, and (c) EDS mapping of PBI-graphene.

The morphology of PBI-graphene was then characterized by FESEM, as shown in Figure 2a. Clearly, the multi-layer structure can be seen in the FESEM image of the PBI-graphene, and is similar to that of the non-functional graphene. The TEM image of PBI-graphene also illustrates the layered structure (Figure 2b). It should be noted that no obvious irregular structures were observed in PBI-graphene, probably suggesting that a homogeneous PBI layer was formed on the surface of the graphene after the surface-initiated polymerization. The composition and element distribution of PBI-graphene was obtained by energy dispersive X-ray spectroscopy (EDS) mapping images of carbon and nitrogen. It is shown in Figure 2c that the distribution of carbon, nitrogen, and oxygen is very uniform, indicating the homogeneous grafting of PBI on the graphene sheets.

Pt nanoparticles were loaded on the graphene and PBI-graphene/XC72 using the polyol reduction method, and TEM images of these supported catalysts are shown in Figure 3. For comparison, commercially available Pt/XC72 was also characterized. As shown in Figure 3 (a, c) and (d, f), the mean particle size and size distribution of Pt/XC72 (2.6 nm, ranging from 1-6 nm) and Pt/PBI-XC72 (2.7 nm, ranging from 1-6 nm) are very similar. However, a higher

number of Pt nanoparticle aggregations were found on the XC72, while the PBI-XC72 assisted the Pt deposition to result in a more homogenous distribution. The agglomeration and poor distribution of Pt nanoparticles became more severe when the unmodified graphene was used as the support, where most Pt particles were populated near the edges of the graphene sheet, while on the basal plane of the graphene sheet, hardly any Pt particles could be found. The average primary particle size of Pt/graphene is calculated to be about 3.5 nm with a wide size distribution ranging from 1 nm to 8 nm, as shown in Figure 3 (g, i). In sharp contrast, it is shown in Figure 3 (j, i) that PBI-graphene enables a much more uniform distribution of Pt nanoparticles across the whole functional graphene sheet, leading to a narrower size distribution from 1 nm to 6 nm, averaging at ca. 3.6 nm. It has been reported that landing of the nanoparticles on the carbon supports favors those sites where the defects or kinks are present.[44] On the other hand, small Pt clusters in the early stages of synthesis tend to form and grow to larger particles in order to reduce their surface energy. The heterogeneity of unmodified XC72 and graphene leads to the non-uniform surface chemistry and the weak bonding strength with Pt clusters; thus, the poor distribution of the Pt nanoparticles was observed. On the contrary, the positively-charged benzimidazole functional groups can provide homogenous nucleation sites for attracting negatively-charged Pt precursor complex ions (PtCl_6^{2-}), which promotes the uniform landing of Pt precursor ion complexes/particles on the surface of PBI-XC72 and graphene.

Figure 3. TEM images and histograms of (a, b) commercial Pt/XC72, (c, d) Pt/PBI-XC72, (e, f) Pt/graphene, (g, h) Pt/PBI-graphene.

Electrochemical measurements were conducted by cyclic voltammetry (CV) at a scan rate of 20 mV/s in N_2 -saturated 0.1 M HClO_4 (Figure 4a). The ECSA of the catalysts is calculated from measuring the integration of the areas of hydrogen adsorption-desorption charges (0.05-0.4 V) after double-layer correction,[45, 46] and is summarized in Table 2. The ECSA for Pt/XC72, Pt/PBI-XC72, Pt/graphene, Pt/PBI-graphene, and Pt/PBI-graphene + FCB are 49.2, 57.6, 34.7, 39.8, and 43.3 $\text{m}^2/\text{g}_{\text{Pt}}$, respectively. The higher surface area of Pt/PBI-XC72 over Pt/XC72 can

be attributed to the smaller amount of agglomeration observed in TEM (Figure 3a and d), since the joined Pt nanoparticles will lose some active sites when participating in the reaction. Interestingly, with the insertion of FCB, Pt/PBI-graphene + FCB recovered some ECSA, suggesting the use of FCB can enlarge the gaps of the graphene sheets, allowing more exposure of the Pt nanoparticles. ORR polarization curves were obtained on RDE in O₂-saturated 0.1 M HClO₄ at a rotation rate of 1600 rpm, as shown in Figure 4b. Mass-transport-corrected kinetic current at 0.9 V vs. RHE was calculated according to the Levich–Koutecky equation and summarized in Table 2. Compared with commercial Pt/XC72, Pt/PBI-XC72 displayed a higher current at 0.9 V vs. RHE. However, graphene- and PBI-graphene-supported Pt nanoparticles exhibit a lower mass activity of 94 and 101 mA/mg_{Pt} than the Pt/XC72 activity of 149 mA/mg_{Pt}. In addition, the limiting currents on the RDE of the Pt/graphene and the Pt/PBI-graphene were much lower than that of Pt/XC-72 catalyst. This is mainly caused by the poor mass transport within the restacked graphene sheets, which possess the slit-shape micro-pores of only several nm.[47] These small micro-sized pores greatly inhibit the diffusion of O₂ within the catalyst layer approaching the active sites of the Pt nanoparticles, thereby decreasing the reduction rate of the O₂. Recently, it has been shown in our work that carbon black particles can be inserted between the graphene sheets and act as spacers to effectively prevent graphene-sheet restacking.[48-50] In this work, benzene sulfonic acid-functionalized carbon black (FCB, SO₃H-EC300) was, therefore, chosen as the spacer for Pt/PBI- graphene because of the potential electrostatic interaction between the positively-charged benzimidazole groups on PBI and the negatively-charged SO₃H groups on carbon blacks. It was discovered that the mass activity of Pt/PBI-graphene increased to 183 mA/g_{Pt} after mixing well with the FCB particles. These results suggest that the insertion of FCB particles as spacers between graphene sheets can significantly prevent graphene restacking and enhance the mass transport of reactant molecules within the Pt/PBI-graphene catalyst layers.

To examine the stability of Pt nanoparticles on different carbon supports, accelerated degradation tests (ADT) were performed by potential cycling between 0.6 V and 1.2 V vs. RHE for 1000 cycles at a scan rate of 20 mV/s in N₂-saturated 0.1 M HClO₄. ECSAs calculated based on hydrogen adsorption and desorption were determined after each 200 cycles. Figure

5a and Table 2 summarize the changes in the ECSAs through ADT. It is shown in Figure 5a that the ECSA of commercial Pt/XC72 drops to 63.1% of its initial ECSA, whereas for Pt/PBI-XC72, the ECSA drops slightly slower to 69.4%. Due to the highly graphitic content of the graphene supports, enhanced stability of Pt/graphene was observed with 73.2% of the initial surface area retained after 1000 cycles. The further improved stability seen on Pt/PBI-graphene (82.6% retained) and Pt/PBI-graphene + FCB (83.0 % retained) is the result of PBI functionalization. ORR activity after ADT was also measured for all the samples on the RDE in O₂-saturated 0.1 HClO₄. As shown in Figure 5b and Table 2, the mass activity of Pt/PBI-XC72 is 141 mA/mg_{Pt} at 0.9 V vs. RHE, which is much higher than that of the commercial Pt/XC72 (88 mA/mg_{Pt}). Similarly, Pt/PBI-graphene and Pt/PBI-graphene + FCB remains 76 mA/mg_{Pt} and 124 mA/mg_{Pt}, respectively, both higher than the Pt/graphene (69 mA/mg_{Pt}). To study the mechanism of durability improvement, TEM was carried out to study the morphological changes of the different catalysts before and after ADT. Figure 3 presents the TEM images and corresponding particle size distribution of commercial Pt/XC72 (b, c), Pt/PBI-XC72 (e,f), Pt/graphene (h, i) and Pt/PBI-graphene (k, l), respectively. Notably, the Pt nanoparticles deposited on pure XC72 and graphene demonstrated significant growth, and most Pt nanoparticles were found to agglomerate and join together. Specifically, the size of the Pt/XC72 increased from 2.7 nm to 4.2 nm, and the size of the Pt/graphene increased from 3.5 nm to 5.2 nm. However, only a slight change in particle size and size distribution were found on Pt/PBI-XC72 (from 2.6 nm to 3.4 nm) and Pt/PBI-graphene (from 3.6 nm to 3.7 nm) after ADT. This further verifies the benefit of PBI functional groups that can strengthen the interaction between carbon supports and Pt nanoparticles and suppress growth and migration/coalescence of Pt nanoparticles.

The interaction between PBI-grafted supports and Pt was revealed by XPS. Figure 6 showed XPS Pt 4f spectra of Pt/XC72, Pt/PBI-XC73 Pt/graphene, and Pt/PBI-graphene. The Pt 4f peaks were quantitatively deconvoluted and the relative ratio of the Pt(0), PtO, and PtO₂ are summarized in Table 3. Three peaks of Pt 4f_{7/2} at around 71.3, 72.1, and 73.6 eV are assigned to Pt metal, PtO, and PtO₂, respectively.[42] The presence of Pt oxide peaks results from the electron transfer from the Pt to the carboxyl and carbonyl groups (strong electron-withdrawing groups) on the carbon black and the hydrazine-reduced graphene

oxide.[51] It can be seen in Table 3 that the ratio of Pt oxides in Pt/PBI-XC72 (42.9%) and Pt/PBI-graphene (43.7%) was lower than those in Pt on unmodified supports (44.8% for Pt/XC72 and 48.9% for Pt/graphene). There are probably two reasons. One is that during the polymerization of PBI, the carboxyl groups may have reacted with 3,3'-diaminobenzidine, weakening the electron withdraw effect. The other possibility is that PBI may have served as an electron donor due to the abundance of lone electron pairs from imine groups. Therefore, the XPS results suggest the presence of a strong interaction between the PBI and the Pt nanoparticles. This strong interaction plays an important role in preventing Pt migration/agglomeration during ADT.

Table 2. ECSA and ORR activity of Pt/PBI-XC72, graphene, PBI-graphene, and Pt/PBI-graphene before and after ADT

Sample	ECSA ($\text{m}^2/\text{g}_{\text{Pt}}$)			Mass activity ($\text{mA}/\text{mg}_{\text{Pt}}$) at 0.9 V vs. RHE		
	Before ADT	After ADT	ECSA Loss	Before ADT	After ADT	Activity Loss
Pt/XC-72	49.2	30.5	38%	149	88	40.9%
Pt/PBI-XC72	57.6	39.6	31.2%	214	141	34.1%
Pt/graphene	34.7	25.4	26.8%	94	69	26.6%
Pt/PBI-graphene	39.8	32.7	17.8%	101	76	24.8%
Pt/PBI-graphene + FCB	43.3	33.8	21.9%	183	124	32.2%

Figure 4. (a) CV curves in N_2 -saturated 0.1 M HClO_4 , 20 mV/s and (b) ORR polarization curves in O_2 -saturated 0.1 M HClO_4 , 20 mV/s.

Figure 5. (a) ECSA and (b) ORR retention of Pt nanoparticles on different carbon supports during ADT tests cycled between 0.6 V and 1.2 V in N_2 -purged 0.1 M HClO_4 , 20 mV/s.

Figure 6. XPS Pt 4f profiles of (a) Pt/XC72, (b) Pt/PBI-XC72, (c) Pt/graphene, and (d) Pt/PBI-graphene.

Table 3. Relative ratio of the Pt 4f_{7/2} components for the different catalysts

	(Pt) 71.3 eV	(PtO) 72.1 eV	PtO ₂ (73.6 eV)
Pt/XC-72	55.2%	32.5%	12.3%
Pt/PBI-XC72	57.1%	30.3%	12.6%
Pt/graphene	51%	32.3%	16.6%
Pt/PBI-graphene	56.3%	27.7%	16%

Figure 7. H₂/O₂ PEMFC polarization curves recorded with different cathode catalysts (0.1 mg_{Pt}/cm²): (a) commercial Pt/XC72 and Pt/PBI-XC72; (b) Pt/graphene, Pt/PBI-graphene, and Pt/PBI-graphene + FCB at 80 °C, 3 bar.

Figure 8. TEM of (a) Pt/PBI-graphene inserted by FCB as the spacer in between the graphene sheets and (b) their pore size distribution based on N₂ adsorption and desorption.

Figure 9. H₂/O₂ PEMFC polarization curves recorded after accelerated stress tests (ASTs) with cathode catalysts of (a) commercial 20 wt.% Pt/XC72 and (b) Pt/PBI-Graphene + FCB, 30 wt.%/. The voltage retention normalized with respect to initial performance after 10, 20, 100, 200, 500, and 1000 cycles is shown in (c).

Fuel cell testing was conducted to evaluate the H₂/O₂ PEMFC performance with various cathode catalysts. The similar mass activity of 403 mA/mg_{Pt} at 0.9 V could be achieved on both Pt/XC72 and Pt/PBI-XC72 cathode catalysts, as shown in Figure 7a, while at a higher current density of > 500 mA/cm², Pt/PBI-XC 72 shows slightly higher activity than Pt/XC72. In the case

of the MEA results of the graphene-based cathode (Figure 7b), it is interesting to note that in the absence of a spacer being inserted, the re-stacking of graphene sheets buries the Pt nanoparticles in between the graphene sheets such that the reactant gases and H^+ conductive ionomer have no access to the surface of the Pt nanoparticles, consequently resulting in the loss of ECSA of the catalyst particles and the decreased Pt utilization, and, thereby, the rapid drop of the polarization curve. However, it is hypothesized that the separation of the graphene sheets from the face-to-face restacking by adding the FCB particles as spacers can effectively create the pores/channels that would greatly facilitate the O_2 being fluxed in and H_2O being fluxed out from the Pt active sites during the operation of the fuel cell. To prove this hypothesis, TEM and nitrogen gas sorption test of Pt/PBI-graphene + FCB were performed to characterize the successful insertion of FCB and to better understand the role of FCB in improving mass transport. It is shown in Figure 8a that FCB particles are sandwiched in between graphene sheets as indicated by the arrow, and pore sizes ranging from 10 nm to 25 nm are created when FCB particles are inserted (Figure 8b). This improvement gave rise to the significant increase of the limiting current of Pt/PBI-graphene from ca. 500 mA/cm^2 to 2000 mA/cm^2 and a comparable PEMFC performance for both Pt/PBI-graphene + FCB and commercial Pt/XC72. On the other hand, the presented IR drop (Figure 7) is mainly attributed to the ohmic loss because of slower H^+ conductivity of the Nafion ionomer matrix within the catalyst layer. The phosphoric acid (H_3PO_4)-doped PBI functional groups could collaborate with the Nafion ionomer to allow fast H^+ hopping, thus leading to the lower IR drop observed on Pt/PBI-XC72 and Pt/PBI-graphene as compared with Pt/XC72 and Pt/graphene, respectively, as shown in Figure 7.

The polarization curves recorded after accelerated stress tests (ASTs) that were carried out through sweeping from 1.0 V to 1.5 V for 10, 20, 100, 200, 500 and 1K cycles are shown in Figure 9. The PEMFC performance of the commercial Pt/XC72 cathode decreased much faster than that of the Pt/PBI-graphene + FCB cathode. At the end of 1K cycles, the MEA with Pt/XC72 could hardly reach 1500 mA/cm^2 , whereas the Pt/PBI-graphene + FCB cathode still maintained $> 60\%$ of its initial voltage at 1500 mA/cm^2 (Figure 9c, Table 4). It is believed that the rapid growth of Pt particles due to the coalescence/agglomeration and Oswald ripening as well as the corrosion of carbon support induced by the sweeping within this high voltage range

(1.0 V to 1.5 V) could take place simultaneously. Although the devolution of these processes is still challenging, these promising results could be largely credited to the better dispersion and strong binding of Pt nanoparticles on PBI functionalized graphene support and the strong corrosion-resistive graphitic structure of graphene. To our best knowledge, these results are one of the earliest works to demonstrate the application of graphene-supported Pt catalysts in the MEA configurations on low-temperature H₂/O₂ PEMFCs.

Table 4. Potential loss @ 1.5 A/cm² of Pt/ XC72 and Pt/PBI-graphene before and after AST

Sample	Potential @1.5 A/cm ² (mV)		
	Before AST	After AST	Potential Loss
Pt/XC-72	673	N/A	673
Pt/PBI-graphene + FCB	580	354	126

4. Conclusion

In summary, we reported a facile preparation of PBI-graphene and XC72 as highly active and durable ORR catalyst supports for low-temperature H₂/O₂ PEMFCs. The successful grafting of PBI on graphene was evidenced by the spectroscopic study. The grafting of PBI onto carbon/graphene surfaces was found to improve the distribution of Pt nanoparticles, and an average particle size of 2.6 nm and 3.6 nm were characterized on Pt/PBI-XC72 and Pt/PBI-graphene, respectively. RDE tests combined with TEM observations revealed that Pt/PBI-XC72/graphene catalysts have excellent intrinsic ORR activity and enhanced durability. The use of the FCB particles as spacers can effectively prevent the restacking of the graphene sheets, consequently, significantly improving the mass transport of gases and ions within the Pt/PBI-graphene catalyst and leading to a comparable MEA performance of the Pt/PBI-graphene catalysts with Pt/XC72. Importantly, ASTs performed in PEMFCs demonstrated the dramatically slower decay of the Pt/PBI-graphene + FCB cathode catalyst as compared to the commercial Pt/XC72. More than 60% of the initial cell voltage at 1500

mA/cm² after 1000 cycles from 1.0 V-1.5 V could be achieved on the Pt/PBI-graphene + FCB, while the Pt/XC72 decayed much more rapidly and could not attain 1500 mA/cm² at the end of the cycling. The reported enhancements of the hybrid Pt/PBI-graphene + FCB are probably due to the favorably strong interaction between Pt particles and PBI-functionalized supports, as well as the stable graphitic structure of graphene. Further optimizations of this hybrid catalyst structures will be the on-going focus with the aim of achieving < 30 mV loss of cell voltage after 5000 cycles of AST in PEMFCs as DOE stated in their requirements for catalyst supports.

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Figure captions:

Figure 1. (a) FT-IR of PBI, PBI- XC72, and PBI-graphene; and (b) XPS N 1s spectrum of graphene, XC72, PBI, PBI-XC72, and PBI-graphene.

Figure 2. (a) FESEM image, (b) TEM image, and (c) EDS mapping of PBI-graphene.

Figure 3. TEM images and histograms of (a, b) commercial Pt/XC72, (c, d) Pt/PBI-XC72, (e, f) Pt/graphene, (g, h) Pt/PBI-graphene.

Figure 4. (a) CV curves in N₂-saturated 0.1 M HClO₄, 20 mV/s and (b) ORR polarization curves in O₂-saturated 0.1 M HClO₄, 20 mV/s.

Figure 5. (a) ECSA and (b) ORR retention of Pt nanoparticles on different carbon supports during ADT tests cycled between 0.6 V and 1.2 V in N₂-purged 0.1 M HClO₄, 20 mV/s.

Figure 6. XPS Pt 4f profiles of (a) Pt/XC72, (b) Pt/PBI-XC72, (c) Pt/graphene, and (d) Pt/PBI-graphene.

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(g)

(h)

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Figure 7. H_2/O_2 PEMFC polarization curves recorded with different cathode catalysts ($0.1 \text{ mg}_{Pt}/\text{cm}^2$): (a) commercial Pt/XC72 and Pt/PBI-XC72; (b) Pt/graphene, Pt/PBI-graphene, and Pt/PBI-graphene + FCB at 80°C , 3 bar.

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